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# NAVORD REPORT

4405

## SYNTHESIS OF NEW HIGH EXPLOSIVES II DERIVATIVES OF 1, 3, 5-TRIBROMO-2, 4, 6-TRINITROBENZENE

FC

1 NOVEMBER 1956



**U. S. NAVAL ORDNANCE LABORATORY**  
**WHITE OAK, MARYLAND**

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SYNTHESIS OF NEW HIGH EXPLOSIVES II,  
DERIVATIVES OF 1,3,5-TRIBROMO-2,4,6-TRINITROBENZENE

Prepared by

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Approved by: DARRELL V. SICKMAN  
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ABSTRACT: In the course of the investigation of the reactions of 1,3,5-tribromo-2,4,6-trinitrobenzene in the search for new high explosives, the preparation and physical properties of 1,3,5-triamino-2,4,6-trinitrobenzene, 1,3,5-tris methylamino-2,4,6-trinitrobenzene, and 1,3,5-tris methylnitramino-2,4,6-trinitrobenzene were studied. The triamino compound was found to be the most stable organic high explosive at elevated temperatures known to the author. It is much superior to our present service explosives, and also possesses a higher crystal density, insensitivity to impact, and a higher detonation velocity than TNT. The tris methylamino and tris methylnitramino derivatives are new to the literature, but offer no advantage over present service explosives. Unsuccessful attempts were made to replace the bromine atoms of the starting material with other explosive contributing groups.

EXPLOSIVES RESEARCH DEPARTMENT  
U. S. NAVAL ORDNANCE LABORATORY  
White Oak, Silver Spring, Maryland

NAVORD Report 4405

1 November 1956

This report is a description of the preparation of derivatives of 1,3,5-tribromo-2,4,6-trinitrobenzene performed under Task NO 800-667/76004/01040. The reliability of the work and the validity of the conclusions are the responsibility of the author and of the Chemistry Division, Explosives Research Department, of the U. S. Naval Ordnance Laboratory. This report is for information only.

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By direction

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SYNTHESIS OF NEW HIGH EXPLOSIVES II,  
DERIVATIVES OF 1,3,5-TRIBROMO-2,4,6-TRINITROBENZENE

INTRODUCTION

This is the second of a series of reports on synthesis of new high explosives. The first of the series were "Preparation and Properties of 2',2',2'-Trinitroethyl-2,4,6-Trinitrobenzoate, Bis(2,2,2-Trinitroethyl)-Alpha Trinitroethyl Succinate, and Bis(2,2,2-Dinitropropyl) Succinate".(1)

We have been studying the chemical reactions of the very reactive explosive intermediate 1,3,5-tribromo-2,4,6-trinitrobenzene in the search for improved high explosives.(2) The chemistry was originally studied in 1888 and then no more work was reported in the literature until recently. Interest was revived in 1,3,5-tribromo-2,4,6-trinitrobenzene in 1948 and again in 1953 in this Laboratory(3). We became most interested in 1,3,5-triamino-2,4,6-trinitrobenzene (TATNB), which was readily prepared from the tribromo compound with alcoholic ammonia. This triamino derivative (TATNB) was found to be quite insensitive to impact, extremely stable to heat, and to have a high crystal density (1.934) and a detonation velocity somewhat superior to TNT at the same percentage of crystal density.

With the revived interest in TATNB, 1,3,5-tris methylamino and 1,3,5-tris methylnitramino-2,4,6-trinitrobenzene were also prepared. The nitramino derivative was sensitive to impact and less stable thermally. Both compounds are new to the chemical literature, but offer no advantage over present service explosives.

One attempt was made to prepare the 1,3,5-tricyano derivative without success. Attempts to react the 1,3,5-tribromo compound with glycine, hydrazine, 5-aminotetrazole, aminoguanidine, and 2,2-dinitropropanol were unsuccessful. Fuerer has reported the successful reaction of glycine with the somewhat similar 1,3-dichloro-2,4,6-trinitrobenzene (4). Hill and Rice of this Laboratory tried unsuccessfully to react trinitroethanol with the similar structure in picryl chloride using aluminum chloride catalysis (5).

EXPERIMENTAL

Preparation of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATNB).

Absolute alcohol (200 ml.) was saturated with ammonia and then 12.5 g. (0.028 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene prepared as described in reference 3 was added. The flask was stoppered and allowed to stand at room temperature for a day. Additional ammonia was bubbled into the mixture which was then heated under reflux for thirty minutes, filtered hot, collecting the insoluble product on a Buchner funnel. The product was washed with water, then alcohol, and dried. We recovered 4.7 g. of TATNB. The product was recrystallized from nitrobenzene. Pure TATNB is reported to melt above 360°C. Qualitative analysis for halogen was negative.

Calculated for  $C_6H_6N_6O_6$ : C, 27.9; H, 2.32; N, 32.55.

Found: C, 28.58, 28.25; H, 2.39, 2.30; N, 31.73, 31.88.

It was found to be almost insoluble in most common solvents which coupled with its high melting point and crystal density probably indicates a high degree of internal hydrogen bonding. The physical properties are given in Table I.

Preparation of 1,3,5-Tris Methylamino-2,4,6-Trinitrobenzene.

Methylamine was bubbled into 100 ml of purified dioxane for ten minutes with stirring, then a solution containing 2.0 g. (0.0042 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene in 50 ml of benzene was added. A yellow precipitate formed and the reaction mixture started to self heat. The temperature was controlled by gentle cooling with an ice bath. The mixture was stirred for two hours after the addition was completed and then allowed to stand at room temperature for four days. The solid was collected on a Buchner funnel, washed with water and dried. The product was recrystallized from nitromethane. The product melted at 266°C with decomposition. A sodium fusion gave a negative test for halogen.

Calculated for  $C_9H_{12}N_6O_6$ : C, 35.95; H, 4.00; N, 28.00.

Found: C, 35.65, 35.69; H, 3.93, 3.69; N, 27.57, 27.22.

The physical properties are given in Table I.

Preparation of 1,3,5-Tris Methylnitromino-2,4,6-Trinitrobenzene.

A 100 ml beaker fitted with a mechanical stirrer and thermometer was charged with 35 ml. of mixed acid of the following composition: 53.4%  $\text{HNO}_3$ , 35.2% 25% oleum, which contained 11.6% free  $\text{SO}_3$ . The acid was cooled to  $15^\circ\text{C}$  and 1.0 g. (0.0033 mole) of 1,3,5-tris methylamino-2,4,6-trinitrobenzene added portionwise. The reaction did not self heat or evolves oxides of nitrogen. The mixture was warmed to  $50^\circ\text{C}$  over a 40 minute period with agitation, cooled to  $5^\circ\text{C}$  and poured on ice. A white precipitate separated immediately and was collected on a sintered glass funnel. The solid was washed with water until acid free and then dried. Recrystallized from an acetone-alcohol mixture, it melted at  $193^\circ\text{C}$ . with decomposition. The yield was 15% of theory based on the methylamino starting material.

Calculated for  $\text{C}_9\text{H}_9\text{N}_9\text{O}_{12}$ : C, 24.8; H, 2.07; N, 28.95.

Found: C, 25.73, 26.25; H, 2.31, 2.33; N, 29.78, 28.94.

The physical properties are tabulated in Table I.

Attempted Preparation of 1,3,5-Tricyano-2,4,6-Trinitrobenzene.

One gram (0.002 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene dissolved in 50 ml of dry benzene was added to 1.0 g. (0.0112 mole) of cuperous cyanide in 10 ml. of methanol and the mixture refluxed four hours. The color of the mixture turned pale green. The reaction mixture was filtered hot, washed with methanol and evaporated to dryness. The residue was taken up in methanol, treated with charcoal, filtered and chilled at  $-20^\circ\text{C}$ . A white crystalline solid (0.46 g.) was isolated which sublimed above  $240^\circ\text{C}$ . Elemental analysis did not agree with that calculated for the desired reaction product. The solid was not characterized further.

Attempted Preparation of 1,3,5-tris 5-Aminotetrazole-2,4,6-Trinitrobenzene.

A mixture of 1.0 g. (0.002 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene and 0.7 g. (0.006 mole) of 5-aminotetrazole in 25 ml. of glacial acetic acid was refluxed six hours and then cooled to room temperature. After standing at room temperature a white solid separated which was isolated and dried, m.  $237-44^\circ\text{C}$ . The solid recrystallized from alcohol, melted at  $297-8^\circ\text{C}$ . A mixed melting point with an authentic sample of the tribromo compound gave no depression. Under the conditions used we did not obtain any of the desired reaction products.

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Attempted Reaction of 1,3,5-Tribromo-2,4,6-Trinitrobenzene  
with Glycine Ethyl Ester Hydrochloride.

A mixture of 4.0 g. (0.008 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene, 2.96 g. (0.03 mole) of sodium carbonate and 2.12 g. (0.03 mole) of glycine ethyl ester hydrochloride in 150 ml. of cellosolve was allowed to stand at room temperature for twenty-four hours. The solid separating was water soluble and appeared to be inorganic when heated over an open flame, and aqueous solution on treatment with HCl did not give a precipitate. The filtrate was acidified, diluted with water and chilled. A solid separated which melted at 285°C. Recrystallization from cellosolve recovered a material melting at 294°C and a mixed melting point with an authentic sample of 1,3,5-tribromo-2,4,6-trinitrobenzene gave no depression. Under the conditions tried we were unable to isolate the desired reaction product.

Attempted Preparation of 1,3,5-Trihydrazino-2,4,6-Trinitrobenzene.

A solution of 2.0 g. (0.003 mole) of the tribromotrinitro compound in 40 ml. of cellosolve was warmed at 70°C and a mixture containing 0.8 ml. (0.014 mole) of 85% hydrazine hydrate and 1.4 g. (0.014 mole) of potassium acetate in 15 ml. of cellosolve was added. The reaction mixture turned a deep red color after warming at 60-70°C for one hour, the reaction mixture was filtered to remove the inorganic salt and the filtrate diluted with water and chilled. An oil separated which we were unable to crystallize, or characterize.

Attempted Preparation of 1,3,5-Tris Aminoguanidine-2,4,6-Trinitrobenzene.

A 50% cellosolve solution containing 7.0 g. (0.026 mole) of aminoguanidine sulfate was treated with an aqueous solution of potassium hydroxide (4.4 g., 0.08 mole) and the potassium sulfate filtered off. The aminoguanidine solution was added to a warm solution of 4.0 g. (0.008 mole) of 1,3,5-tribromo-2,4,6-trinitrobenzene in 150 ml. of cellosolve. The reaction mixture was allowed to stand at room temperature of about twenty-four hours. On chilling a solid separated which after recrystallization from ethanol melted at 125°C. Elemental analysis proved the solid was not our desired reaction product. The solid was not characterized further.

Attempted Preparation of 1,3,5-(2,2-dinitropropyl)-2,4,6-Trinitrobenzene.

A mixture of 0.5 g. (0.002 mole) of 1,3,5-triamino-2,4,6-trinitrobenzene and 0.9 g. (0.006 mole) of 2,2-dinitropropanol were suspended in 25 ml. of concentrated sulfuric acid and

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the mixture warmed slowly to 100°C, where a solution was complete and deep red in color. The solution was poured on ice and chilled. As a solid did not separate, it was assumed that the desired reaction did not take place under these conditions. At elevated temperature the sulfuric acid probably formed a water soluble salt similar to that formed with aniline in sulfuric acid.

TABLE I  
PHYSICAL PROPERTIES

| Compound  | m.p.  | Impact Sensitivity | Vacuum Stability<br>cc gas/48 hrs. 100°C | Density |
|---|-------|--------------------|--|---------|
| 1,3,5-Tribromo-<br>2,4,6-trinitro-<br>benzene             | 296°C | 118 cm.            | Nil                                      | 2.39    |
| 1,3,5-Triamino-<br>2,4,6-trinitro-<br>benzene             | 360°C | >320 cm.           | 0.36/a,b                                 | 1.934   |
| 1,3,5-tris<br>Methylamino-<br>2,4,6-trinitro-<br>benzene  | 266°C | —                  | —  | —       |
| 1,3,5-tris Methyl-<br>nitramino-2,4,6-<br>trinitrobenzene | 193°C | 18 cm.             | 2.55                                     | —       |

/a 6.0 cc in 2 hrs. 260°C (500°F), at 250°C HMX decomposed in a few minutes.  
A mixture of the triamino compound with Ba(NO<sub>3</sub>)<sub>2</sub>/Al @ 250°C gave 4 cc in  
2 hrs., impact sensitivity was 143 cm., σ 0.27 with a 2.5 kg. wt.

/b 11.5 cc in 30 minutes @300°C.

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TABLE II  
DETONATION VELOCITY MEASUREMENTS OF 1,3,5-TRIAMINO-  
2,4,6-TRINITROBENZENE (6)(7)

| <u>Density</u> | <u>Velocity</u><br><u>(Meters/Sec)</u> |
|----------------|--|
| 1.290          | 5380                                   |
| 1.345          | 5628                                   |
| 1.675          | 6550                                   |
| 1.675          | 6575                                   |
| 1.882          | 7035                                   |
| 1.835          | 7220 (95% of crystal density)*         |

\* TNT, 6800 m/sec. at 1.57, 95% of crystal density

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CONCLUSIONS

TATNB was particularly interesting in its resistance to heat, but it did not appear to offer any other advantages over conventional explosives in present day use. The higher cost of preparation would also rule it out as a substitute for any of the present military high explosives, except for special application. TATNB might prove a useful high explosive for use in the war heads of high speed guided missiles or in projectiles carried by jet aircraft where aerodynamic heating is a major problem facing all of the Services today. Present service explosives require elaborate insulation of the warhead and decompose rapidly at temperatures in excess of 200°C (390°F). TATNB appears to be stable for some hours at 260°C (500°F) and such additives as aluminum powder and barium nitrate do not impair this stability. The feasibility of its use in this application is under investigation and the results of the work will be reported at a later date.

The 1,3,5-tris methylamino and 1,3,5-tris methylnitramino-2,4,6-trinitrobenzene do not appear to offer anything useful as new explosives. It is felt that an effort to prepare 1,3,5-tricyano-2,4,6-trinitrobenzene may afford a new and interesting explosive compound, as 2,4,6-trinitrobenzonitrile prepared in this laboratory is known to be a stable compound<sup>(8)</sup>.

We feel that the severe steric hinderance around the bromine atom as well as the tendency toward decomposition in the presence of base obviously limits the scope of the substitution reactions on the tribromo derivative. It is thought that substitution of chlorine for bromine may aid in increasing the scope of the reaction.

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The author wishes to acknowledge the assistance of W. A. Moats and R. L. Beauregard in the synthetic work. The detonation velocity measurements were made by R. H. F. Stresau's group.



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